

Complex Optical Surfaces Formed by Replica Molding Against Elastomeric Masters

Younan Xia, Enoch Kim, Xiao-Mei Zhao, John A. Rogers, Mara Prentiss, George M. Whitesides*

Complex, optically functional surfaces in organic polymers can be fabricated by replicating relief structures present on the surface of an elastomeric master with an ultraviolet or thermally curable organic polymer, while the master is deformed by compression, bending, or stretching. The versatility of this procedure for fabricating surfaces with complex, micrometer- and submicrometer-scale patterns was demonstrated by the production of (i) diffraction gratings with periods smaller than the original grating; (ii) chirped, blazed diffraction gratings (where the period of a chirped grating changes continuously with position) on planar and curved surfaces; (iii) patterned microfeatures on the surfaces of approximately hemispherical objects (for example, an optical surface similar to a fly's eye); and (iv) arrays of rhombic microlenses. These topologically complex, micropatterned surfaces are difficult to fabricate with other techniques.

Replica molding of an organic polymer (for example, polyurethane, polymethylmethacrylate, or epoxy) against an elastomeric master [made, for example, of poly(dimethylsiloxane) (PDMS)], while that master is deformed, provides a strategy for the fabrication of complex micropatterns on surfaces. Deformation of the elastomeric master, followed by replication of the structures present on the surface of the deformed master in the rigid polymer, provides a route to structures that would be impractically difficult to generate through other procedures. Molding and embossing of organic polymers against rigid masters is used to manufacture optically functional microstructures such as diffraction gratings (1) and compact disks (2). The procedure described here differs in the use of an elastomeric master, and important features of the replica structure are generated by the mechanical deformation of this master (3, 4). Deformation of the elastomeric master occurs isotropically, and simple, regular, planar microstructures present on the original surface can be transformed into topologically and spatially complex microstructures in the replica with good preservation of optically relevant characteristics, such as grating regularities and blazings.

In the procedure for replica molding against an elastomeric master under mechanical compression (5, 6) (Fig. 1A), a liquid prepolymer reaction mixture of PDMS is cast against a rigid master whose surface has been patterned in an appropriate relief structure (a diffraction grating or a

more complex structure made by photolithography or micromachining). After curing, the cross-linked PDMS is peeled from the master; its surface replicates the surface of the rigid master. These replicated features are then reconfigured by the mechanical compression of the elastomeric master, and the deformed structure is replicated by the casting of ultraviolet-curable liquid polyurethane (PU) against it. If desired, this procedure can be repeated, with the PU replica used as the starting point, to make structures more complex than can be generated in one cycle (although with some degradation in the quality of the fabricated optical surface).

In the procedure that we used to fabricate diffraction gratings on cylindrical surfaces (Fig. 1B), a thin PDMS master ($\leq 50 \mu\text{m}$ thick) was bent to make conformal contact with a curved surface coated with a thin film of liquid PU. After curing of the PU, the PDMS master was removed to reveal the PU replica on the surface of the cylindrical substrate. A similar procedure was used to produce an approximately hemispherical object having micropatterned relief structures on its surface (Fig. 1C). We mounted a thin PDMS master ($\sim 1 \text{ mm}$ thick) across the end of a hollow glass tube and deformed it by applying positive or negative pressure through the tube. The resulting surface was replicated in PU.

Cross-sectional scanning electron micrographs (SEMs) (Fig. 2, A through C) show a square-wave test pattern produced in PU over several cycles of replication in PDMS, compression, and replication in PU. Using this test structure, we found that two cycles of compression and replication reduced the size of some features (that is, the recessed areas on the master) from $\sim 1.6 \mu\text{m}$ to $\sim 200 \text{ nm}$ and reduced the period of this test pat-

tern from ~ 3.6 to $\sim 1.5 \mu\text{m}$. During the cycles of compression and replication, the dimensions of the recessed areas decreased more than those of the raised areas. The reductions in dimensions that were observed were consistent with the computer-simulated results (Fig. 1A) (7). Because profiles of the relief microstructures on the elastomeric master changed in a predictable and controllable way under mechanical deformation, the master could be fabricated such that the relief microstructures have the proper profiles after deformation. Figure 2B is an expansion of the smallest features ($\sim 200 \text{ nm}$) that have been made; a larger field view of these features (Fig. 2C) illustrates their regularity. This procedure thus allows the formation of gratings with a range of values of the period starting from a single master.

By compressing one end of the elastomeric

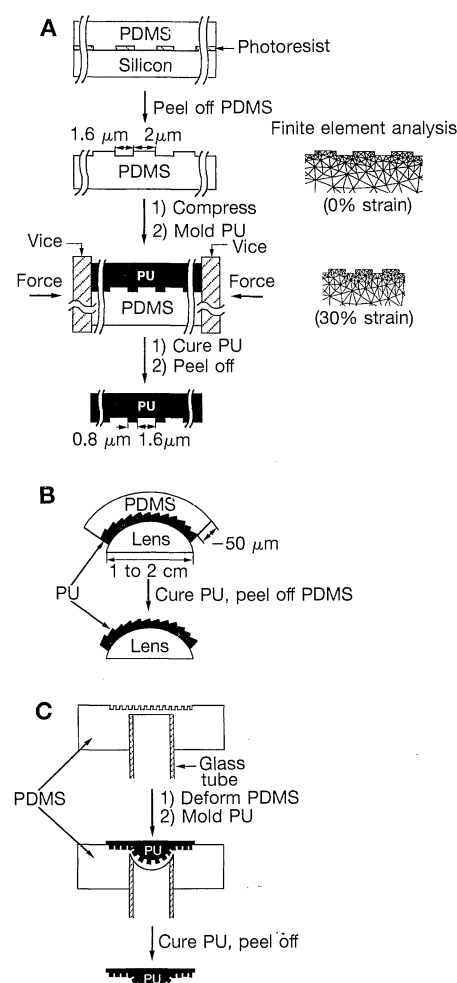


Fig. 1. Schematic procedures for molding-replication against an elastomeric master under (A) mechanical compression, (B) bending, and (C) stretching. In the finite element analysis of the material response of the PDMS master to mechanical compression, it was assumed that the top surface of the PDMS master was stress-free and that the Poisson's ratio of PDMS was 0.4 [see (7)].

Y. Xia, E. Kim, X.-M. Zhao, J. A. Rogers, G. M. Whitesides, Department of Chemistry, Harvard University, Cambridge, MA 02138, USA.
M. Prentiss, Department of Physics, Harvard University, Cambridge, MA 02138, USA.

*To whom correspondence should be addressed.

master more than the other, we were able to fabricate a chirped diffraction grating—a grating whose period changes continuously with position (8). More interestingly, the shape of the diffracting elements was largely preserved in this process: if we used a blazed grating as the starting master, the resulting chirped PU replica was also a blazed grating (Fig. 3, A and B). The period (Λ) of this chirped, blazed grating changed continuously from a value of ~ 1.55 to ~ 1.41 μm over a distance of ~ 0.9 cm: the rate of chirping ($d\Lambda/dz$) was $\sim 1.6 \times 10^{-5}$. This grating was characterized in transmission at normal incidence. Figure 3C shows the diffraction patterns (the zero-order and the two first-order peaks) of the PDMS master, its PU replica, and the chirped PU grating. The PDMS grating and its PU replica were not operated in the blazing condition. The two first-order diffraction peaks had similar intensities (9).

The relief pattern on the surface of a planar, chirped, blazed grating could be easily transferred onto a curved surface by rep-

lica molding against a thin PDMS master cast from this planar grating (Fig. 1B). Figure 4A is an optical photograph of a chirped, blazed grating that was fabricated on a negative cylindrical lens [a concave grating (1)]. The shape of the diffracting elements was preserved in the process of bending and replication (Fig. 4B).

Figure 4, C and D, shows SEM images of a hemispherical PU object with a pattern of relief microfeatures on its surface (a fly's eye; Fig. 1C) (10). The shape of this polymeric object can be easily tuned by changing the thickness of the PDMS master, the applied pressure, or both. A range of different relief patterns could be made; the smallest feature had a size of ~ 1.5 μm .

In addition to reducing the size of features, mechanical compression can also be

used to change their shape while preserving size (Fig. 4, E and F) (11, 12). One-dimensional compression changed the shape of the microlenses from square to rhombic. We could readily fabricate microlenses with different geometric shapes and therefore different focusing characteristics.

Molding-replication against a deformed elastomeric master is a strategy for making topologically complex structures with micropatterned surfaces: it allows the size and shape of features present on the surface of the master to be changed by using mechanical compression, bending, stretching, or a combination of these techniques, and generates complex structures with variable feature sizes from simple, regular structures. The highly isotropic deformation in the shape of relief patterns on the master permits micropatterned structures to be formed with gradients in size and shape.

We believe that this strategy will have broad application in applied optics: the chirped, blazed grating on a nonplanar surface is a good example of a structure that would be difficult to produce by other procedures. It may also be useful in other applications that use complex micropatterned surfaces [for example, cell culture with anchorage-dependent cells (13), studies relating interfacial structure to properties such

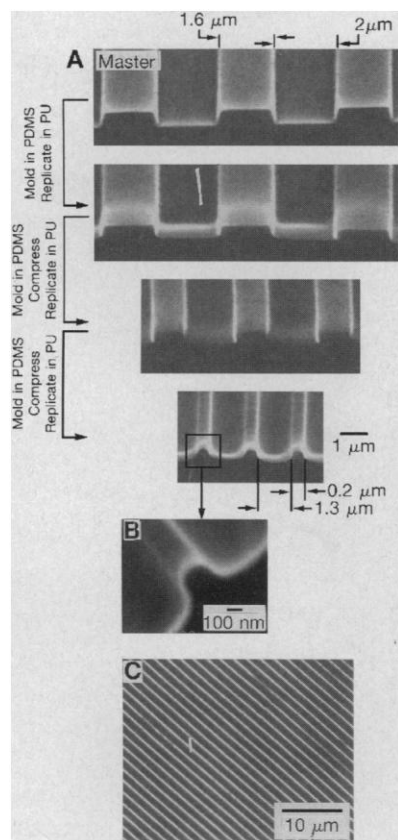


Fig. 2. (A) Cross-sectional SEMs of the original master (generated in a photoresist film coated on a silicon wafer by photolithography) and the PU replicas generated after different cycles of replication in PDMS, compression, and replication in PU. Gold (~ 60 nm thick) was sputtered onto the PU replicas before the SEM images were taken. (B) An enlargement and (C) a larger field view of the smallest features (~ 200 nm) that have been fabricated by this procedure.

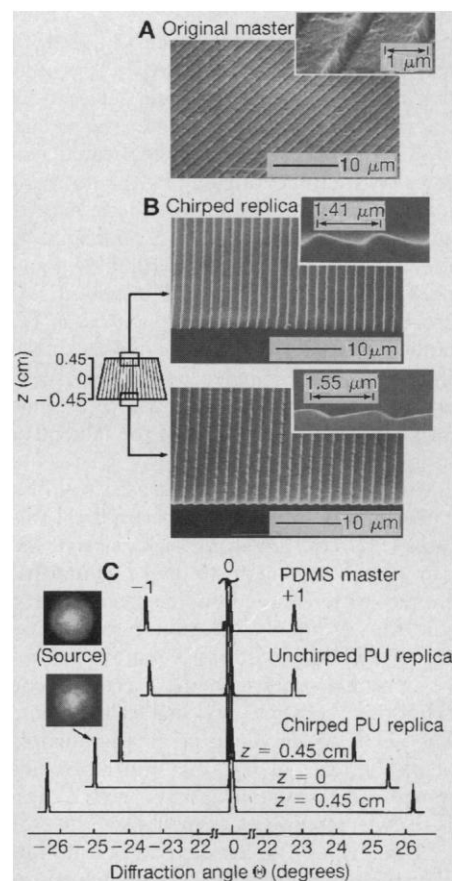


Fig. 3. Cross-sectional SEMs of (A) a commercial blazed diffraction grating and (B) selective regions of a planar, chirped, blazed PU replica grating that was fabricated by molding against the PDMS master while it was compressed asymmetrically. The fact that the two ends of the blazed grating seem to have different orientations for the blazing is an artifact of the orientation of the grating when the micrograph was taken. (C) Diffraction patterns from the PDMS master, its PU replica, and the chirped PU grating. A He-Ne laser (wavelength $\lambda = 632.8$ nm) was used. The insets show images of the laser source and one first-order diffraction spot, respectively.

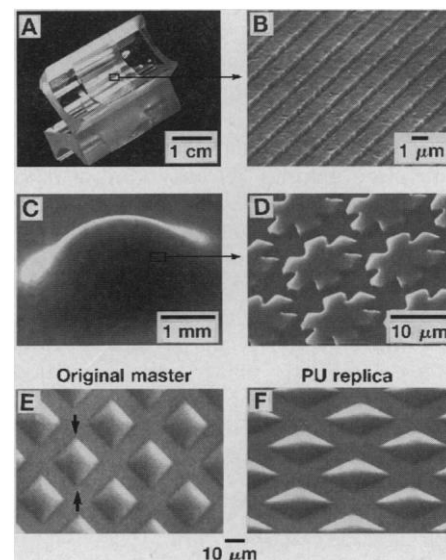


Fig. 4. (A) An optical photograph of the chirped, blazed grating fabricated on a negative cylindrical lens. (B) The SEM micrograph of this grating. (C and D) SEMs of a polymeric dome-shaped object and the relief patterns on its surface. (E) The SEM image of an array of square PU microlenses assembled on a silver substrate with patterned hexadecanethiolate self-assembled monolayers used as the template. (F) The SEM of an array of rhombic PU microlenses that was produced by molding-replication against the PDMS master cast from the PU structure of (E) under one-dimensional compression along the vertical direction (as indicated by arrows).

as wetting or adhesion (14), and fabrication of microelectromechanical systems (15) and sensors (16)].

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6. Sylgard 184 (Dow Corning, A:B = 1:20) silicone elastomer was used. It was cured at room temperature for ~2 hours and then at ~65°C for ~6 hours. Ultra-violet-curable PU (NOA-73; Norland Products, New Brunswick, NJ) was cured with a medium-pressure mercury vapor lamp (450 W, ACE Glass, Louisville, KY) for ~20 min, with the lamp positioned ~2 cm from the sample. Blazed gratings were obtained from Edmund Scientific.
7. Computer simulation was done with PDEase2, Finite Element Analysis for Partial Differential Equations, version 2.5.2.
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9. This different behavior can be attributed to their difference in period. When a blazed grating is used in transmission, each groove acts as a prism, and the condition for blazing is given by $\Lambda \tan \phi [n - (1 - \lambda^2/d^2)^{1/2}] = \lambda$ (1), where Λ is the period of the grating, n is the refractive index of the grating material, and ϕ is the facet angle. The PDMS master replicated from the commercial grating blazes in the near-infrared region (~1000 nm); the chirped grating is expected to blaze at shorter wavelengths (that is, closer to the wavelength of the visible laser that was used) because the period of the chirped grating is shorter than that of the PDMS master. The relation between the diffraction angle θ and z can be described by $\theta = \sin^{-1}[\lambda/(z d \Lambda/dz + \Lambda_0)]$, where Λ_0 is the period at $z = 0$; the diffraction angles so calculated were in agreement with the measured values.
10. PDMS prepolymer reaction mixture (Sylgard 184, A:B = 1:15) about 1 mm thick was poured over a rigid master that was placed in a plastic petri dish. The PDMS was cured in an oven for ~5 hours at ~65°C. A glass tube (~4 cm long) was then vertically placed on the top of the cured PDMS, and PDMS prepolymer reaction mixture (A:B = 1:10) ~0.5 cm thick was added. The glass tube was pressed against the first layer of PDMS with Scotch tape, and no fresh PDMS prepolymer reaction mixture could enter the glass tube. The whole system was cured at room temperature for ~12 hours and then at ~65°C for ~5 hours. Adhesion between the second layer of PDMS and the glass was good.
11. The master was fabricated according to a three-stage procedure (5, 12): (i) the first used microcontact printing to form lines of hexadecanethiolate on a silver surface; (ii) the second used microcontact printing to print lines of hexadecanethiolate perpendicular to the lines of (i) on the same silver surface; (iii) the third assembled liquid prepolymer reaction mixture of PU onto the bare regions of the silver surface and cured the liquid PU under an ultraviolet light.
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Cytoplasmic Tail-Dependent Localization of CD1b Antigen-Presenting Molecules to MHCs

Masahiko Sugita, Robin M. Jackman, Elly van Donselaar, Samuel M. Behar, Rick A. Rogers, Peter J. Peters, Michael B. Brenner, Steven A. Porcelli*

CD1 proteins have been implicated as antigen-presenting molecules for T cell-mediated immune responses, but their intracellular localization and trafficking remain uncharacterized. CD1b, a member of this family that presents microbial lipid antigens of exogenous origin, was found to localize to endocytic compartments that included the same specialized subset of endosomes in which major histocompatibility complex (MHC) class II molecules are proposed to bind endocytosed antigens. Unlike MHC class II molecules, which traffic to antigen-loading endosomal compartments [MHC class II compartments (MIICs)] primarily as a consequence of their association with the invariant chain, localization of CD1b to these compartments was dependent on a tyrosine-based motif in its own cytoplasmic tail.

Non-MHC encoded CD1 molecules have been implicated as a family of β_2 -microglobulin-associated nonpolymorphic polypeptides that function in antigen presentation. Identification of a T cell line that recognizes mycolic acid, a complex fatty acid from the mycobacterial cell wall, in a CD1b-restricted fashion (1) and the subsequent derivation of two other CD1b-restricted T cell lines that recognize lipoarabinomannan from *Mycobacterium leprae* demonstrate the capability of CD1b to present exogenously derived microbial lipid antigens (2). These CD1b-restricted lipid and glycolipid antigens appear to require intracellular processing in acidic compartments, as do peptide antigens presented by MHC class II molecules (1, 2). Thus, it is proposed that CD1b molecules, despite their MHC class I-like protein structure (3), might traffic to endocytic compartments, including those in which MHC class II molecules encounter endocytosed antigens.

As was consistent with this hypothesis, CD1b induced on peripheral blood monocytes by stimulation with granulocyte-macrophage colony-stimulating factor (GM-CSF) and in-

terleukin-4 (IL-4) (1) was found by immunofluorescence microscopy not only on the cell surface, but also in peripherally distributed vesicles into which Texas Red-conjugated ovalbumin was endocytosed (Fig. 1). Double labeling of CD1b⁺ monocytes with antibodies against lysosome-associated membrane protein 1 (LAMP-1, a marker of late endosomes and lysosomes) showed that most CD1b⁺ endocytic vesicles coexpressed this protein (4). Furthermore, most CD1b⁺ vesicles in monocytes, as well as in a CD1b-transfected human B cell line (C1R/CD1b) (1) stained with antibodies to MHC class II molecules (4). This profile was characteristic of the recently described MHC class II compartment (MIIC) of specialized or "professional" antigen-presenting cells, which is the proposed site at which newly synthesized MHC class II molecules accumulate and acquire exogenous peptide antigens (5-7).

Previous studies using electron microscopy have identified MIICs morphologically as electron-dense structures, characterized by extensive membrane invaginations producing either a multivesicular or multilamellar appearance (5-7). Immunogold-labeled transmission electron microscopy of ultrathin cryosections of GM-CSF- and IL-4-stimulated monocytes revealed expression of CD1b in MHC class II-positive dense multilamellar organelles (Fig. 2A), which were characteristic of MIICs previously observed in mononuclear phagocytes (8). As was consistent with the localization of CD1b in

M. Sugita, R. M. Jackman, S. M. Behar, M. B. Brenner, S. A. Porcelli, Lymphocyte Biology Section, Division of Rheumatology and Immunology, Brigham and Women's Hospital, Harvard Medical School, Boston, MA 02115, USA. E. van Donselaar and P. J. Peters, Department of Cell Biology and Institute of Biomembranes, Faculty of Medicine, University of Utrecht, Utrecht, Netherlands. R. A. Rogers, Department of Environmental Health, Harvard School of Public Health, Boston, MA 02115, USA.

*To whom correspondence should be addressed.